
CLAIMS

[Claim(s)]

[Claim 1] A measuring method of hair moisture characterized by comprising the following.

An analytical curve creation process of irradiating with a near infrared ray to two or more hair samples of moisture content known, asking for two or more diffuse reflection or penetration reflection spectrum data, and preparing an analytical curve of a moisture content of hair.

A moisture content measuring process which irradiates with a near infrared ray directly to a test subject's hair, asks for diffuse reflection or penetration reflection spectrum data, and measures a moisture content of hair using this analytical curve.

[Claim 2] A measuring method of the hair moisture according to claim 1 preparing said analytical curve in said analytical curve creation process using a partial-least-squares-regression-analysis method.

[Claim 3] Pretreatment which differentiates a predetermined degree in said analytical curve creation process to said two or more diffuse reflection or penetration reflection spectrum data, And a measuring method of the hair moisture according to claim 1 including a stage of performing at least one pretreatment in pretreatment which gives MSC in diffuse reflection or penetration reflection spectrum data of this plurality.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the measuring method of hair moisture.

[0002]

[Description of the Prior Art] Hair is divided into the scapus pili (hair shaft) of the portion which has come out to the skin surface, and the hair root (hair root) of the portion which has entered into the inside of the skin. Hair comprises same keratin as the main ingredients of the horny layer of the skin. Keratin is protein accumulated into epidermal cells in a biochemical definition.

[0003] The moisture of hair exists with the gestalt of the absorbed water to protein. Hair has the character which absorbs water and the moisture content of hair changes with environmental factors of the external world. Under the usual environment, the moisture content of hair is about 10 to 15%.

[0004] When hair is touched by hand, the feel liked by the user of hair cosmetics is a soft feel carried out gently of being smooth. especially the moisture content in hair has contributed -- the user of hair cosmetics asks for ** strongly gently.

It is important also when choosing hair cosmetics.

[0005]As a method of carrying out the quantitative analysis of the moisture content in hair, conventionally, (1) Measure the weight of the hair dried at the elevated temperature (not less than 100 **) after creating the bunch of hair and measuring the weight under certain environment, Use the reaction of a weight method (weighing method), and (2) water molecules and the iodine compound which compute the rate of water weight over dry hair, and the generated molecular iodine (I_2) is electrolyzed, The Karl Fischer's method which computes the number of mols of water from the current amount which flowed, and measures a moisture content, the electrical conductance measuring method which measures the electric conductivity for two places of (3) hair, and by forcing (4) ATR-crystal probe, The inside infrared spectrum was measured and the ATR-infrared (inside infrared rays) spectroscopy etc. which presume a moisture content by the intensity ratio of the band by OH to an amide band have been used.

[0006]By the way, the near infrared ray of a wavelength band (0.8 micrometer - 2.5 micrometers), 1) Since water absorption intensity becomes weak by near-infrared rays compared with 3 infrared rays applicable to the sample of various states, such as two solids, a granular material, textiles, a fluid, and a gas, which do not damage a sample since the low electromagnetic waves of energy are used, it has an advantage, like analysis with solution can be performed. For this reason, a near infrared ray is beginning to be used in various fields in recent years including an agricultural field. Also in the somatometry field, it is observed as non-invasion and pollution-free analytical skills, examination towards utilization is advanced (IFSCC Yokohama convention gist 1132-1146 (1992).) J. Cosmet.Sci., 51 (3), 183-192 (2000), Applied Spectrosc., 46 (5), 875-878 (1992), etc.

[0007]

[Problem(s) to be Solved by the Invention]However, the conventional moisture content measuring method of above-mentioned (1) - (4), Even if it is necessary to carry out cutting extraction of the hair sample before measurement, and it is not what is called nondestructive measurement or it is nondestructive measurement, Like electrical conductance measurement, it is a relative comparison of a moisture content and there are various faults of an absolute value not being measured, or it being used for local measurement, such as near the surface of hair, and being unable to measure the amount of mean moisture of the whole hair again.

[0008]The hair cosmetics user who changes hair coloring and the color of his hair called bleach has a large number in recent years, and these persons' hair has received various damages accompanying hair coloring bleach etc. For this reason, since the melanin contained in hair by birth and the coloring matter of hair coloring have absorption of energy in a light range when it tries to carry out the quantitative analysis of the moisture content of hair using the absorbance of the above-mentioned near infrared ray, The hair from which a color differs has the necessity of the baseline of the near infrared ray contiguous to a light range changing, therefore taking amendment of a baseline, etc. into consideration. When it is going to measure the moisture content of hair using the spectrum of light which the near infrared ray penetrated or reflected, while there is a problem from which a baseline changes like the time of the above-mentioned spectrometry, In order that a near-infrared absorption signal may treat harmonics, as compared with infrared rays, it is very weak, and also it has the fault that attribution of a

band is not clear, and has not resulted [from the viewpoint] in the utilization which obtains the required accuracy of measurement.

[0009]In light of the above-mentioned problems, this invention is a thing.

What is called cutting extraction target nondestructive measurement can be performed. It is being able to measure not the relative comparison of a moisture content but an absolute value moisture content, and being able to measure the amount of mean moisture of the whole hair instead of the local measurement near the surface of hair etc., and providing further again the measuring method of the hair moisture which can perform these measurement by a simple method.

[0010]An object of this invention is to provide the measuring method of the hair moisture which can be measured in high accuracy, without receiving influence in external change factors, such as a damage of hair.

[0011]

[Means for Solving the Problem]This invention is characterized by a measuring method of hair moisture comprising the following.

An analytical curve creation process of irradiating with a near infrared ray to two or more hair samples of moisture content known, asking for two or more diffuse reflection or penetration reflection spectrum data, and preparing an analytical curve of a moisture content of hair.

A moisture content measuring process which irradiates with a near infrared ray directly to a test subject's hair, asks for diffuse reflection or penetration reflection spectrum data, and measures a moisture content of hair using this analytical curve.

[0012]Measuring [beforehand / a moisture content]-using how to have been established here for measuring moisture content with moisture content known ****. A method of using for water measurement of the conventional skin as such a measurement technique, for example, etc. can be mentioned. In order to prepare an analytical curve, it can choose from among these techniques suitably, and can use. The near infrared ray can choose suitably a thing of a wavelength range which contains wavelength of 1.45 micrometers and/or 1.93 micrometers among the wavelength ranges of 0.8-2.5 micrometers, and it can be used for it.

[0013]By the above-mentioned composition of this invention, by measuring hair moisture using diffuse reflection or a penetration reflection spectrum of a near infrared ray with short wavelength compared with inside infrared rays. Since what is called nondestructive measurement that does not have to carry out cutting extraction of the hair before measurement can be performed, not a relative comparison of a moisture content but an absolute value moisture content can be measured and a near infrared ray has the character in which substance permeability is high, The amount of mean moisture of the whole hair instead of local measurement, such as near the surface of hair, can be measured, and these measurement can be performed by a simple method further again.

[0014]In this case, in said analytical curve creation process, said analytical curve is prepared using a partial-least-squares-regression-analysis method (partial least square method: partial least squares regression), Or pretreatment which differentiates a predetermined degree again to said two or more diffuse reflection or penetration reflection spectrum data, and diffuse reflection or penetration reflection spectrum data of

this plurality -- MSC (multiplicative scatter correction: -- multiplication -- sex dispersion correction.) A moisture content of hair can be measured in high accuracy, without receiving influence in external change factors, such as a damage of hair, by using what is called these chemometrics techniques, if a stage of performing at least one pretreatment in pretreatment which performs multiple scattering correction is included.

[0015]

[Embodiment of the Invention] The suitable embodiment (henceforth this example of an embodiment) of the measuring method of the hair moisture concerning this invention is described below with reference to figures.

[0016] The measuring method of the hair moisture concerning this example of an embodiment can be performed in the procedure below an outline using portable near-infrared spectroscopic analysis devices, such as marketing, for example, SUPEKU TRON tech company make etc., and the near-infrared Blanc Roubaix spectroscopic analysis device.

[0017] A near-infrared spectroscopic analysis device exposes a test subject's hair to the near infrared ray which emitted light using a tungsten halogen lamp as a light source through an optical fiber. The quality of facing makes hair touch the probe at the tip of an optical fiber from on the light reflector with which hair rode as a part of the test subject's hair rode on even light reflectors, such as alumina and gold, at this time, so that it may become vertical to a light reflector.

[0018] The light by which the light which penetrated hair was reflected by the light reflector, penetrated hair again, and diffuse reflection was carried out from hair as penetration catoptric light. It enters into the detector using PbS or a photo-diode through the optical fiber for light-receiving which was combined and was provided in the probe for an exposure as a diffuse reflection. In PbS, the detector can detect the reflection spectrum of the range of 1.1-2.5 micrometers with resolution of 0.5 nm, for example.

[0019] Penetration reflection from a detector, or diffuse-reflectance-spectrum intensity (generally both are uniformly called diffuse-reflectance-spectrum intensity.) Hereafter, it is written as diffuse-reflectance-spectrum intensity also about penetration reflection-spectrum intensity. The embraced electrical signal is generated, amplification processing is carried out and an electrical signal is outputted to a microcomputer. In a microcomputer, the moisture content of hair is outputted using the analytical curve which predetermined pretreatment mentioned later was performed and was stored in the memory and which is mentioned later.

[0020] The measuring method of the hair moisture concerning this example of an embodiment using the above-mentioned near-infrared spectroscopic analysis device is explained. Here, the case where use the former penetration catoptric light among near-infrared penetration catoptric light and a diffuse reflection, and the spectrum (it is hereafter written as a diffuse reflectance spectrum.) of the penetration catoptric light measured is used is explained.

[0021] The process (analytical curve creation process) of the measuring method of hair moisture irradiating with a near infrared ray to two or more hair samples of moisture content known, asking for two or more diffuse-reflectance-spectrum data, and preparing the analytical curve of the moisture content of hair, It consists of a process (moisture content measuring process) of irradiating with a near infrared ray directly to a test subject's hair, asking for diffuse-reflectance-spectrum data, and measuring the moisture

content of hair using the prepared analytical curve.

[0022]First, an analytical curve creation process is explained.

[0023]Under different humidity environment, hair of the various number of times of bleach in an equilibrium situation is used as standard sample hair (hair sample), and is prepared sample number N=90. What is the bleach liquid adjusted the pH to 9.5 with the ammonia solution, carried out bleach processing to 0 times - 6 times, including hydrogen peroxide 3%, and specifically washed moderately the hair of the Japanese woman without hair coloring or the history of a permanent wave was used as standard sample hair. And while measuring a moisture content by the existing water measurement method using such standard sample hair, in accordance with this, diffuse-reflectance-spectrum data (relative diffusion reflection spectrum data) is obtained using a near-infrared spectroscopic analysis device.

[0024]As the existing water measurement method, the weight method used abundantly so far is used, for example. A moisture content is measured about standard sample hair by producing the bunch of about 0.1 g of hair, and measuring the weight of the bunch of hair in a constant temperature/humidity chamber.

[0025]On the other hand, about the same standard sample hair as having presented measurement of the above-mentioned weight method, using a near-infrared spectroscopic analysis device, it irradiates with the near infrared ray of the wavelength range of 1.1-2.5 micrometers, and below near-infrared relative diffusion reflection-spectrum-data < of standard sample hair only calls it relative diffusion reflection spectrum data. > is obtained. An example of relative diffusion reflection spectrum data is shown in [drawing 1](#). In [drawing 1](#), a horizontal axis shows wavelength and . one side and the vertical axis whose unit is NANOMETORU (nm) show the natural logarithm of the reciprocal of the relative diffusion reflectance R. The band of water is observed 1450 nm and near 1930 nm among [drawing 1](#).

[0026]In this example of an embodiment, in order to present analytical curve creation, the above-mentioned relative diffusion reflection spectrum data are pretreated.

[0027]As pretreatment, it goes relative diffusion reflection spectrum data (relative diffusion reflection spectrum) to quadratic differential, and a quadratic differential spectrum (quadratic differential spectrum data) is acquired. After carrying out equalizing processing (Mean Centering) of the measured relative diffusion reflection spectrum beforehand at this time, quadratic differential is carried out and a quadratic differential spectrum is searched for. Here, equalizing processing means searching for the spectrum which consists of average value of all the spectra in each wavelength. An example of a quadratic differential spectrum is shown in [drawing 2](#). This quadratic differential spectrum obtains it by carrying out quadratic differential of the near-infrared reflection spectrum of [drawing 1](#). By quadratic differential, a baseline can be set to 0 (zero) also to which spectrum.

[0028]Here, MSC is further performed as pretreatment using the above-mentioned quadratic differential spectrum. Thereby, amplification (multiplication sex) and offset (additivity) are removed from a quadratic differential spectrum, for example, many problems, such as a problem of the light path length of a measuring device, a shift of offset, and interference, are solved. An example of the spectrum after MSC is shown in [drawing 3](#). The spectrum after this MSC amends and acquires the quadratic differential spectrum of [drawing 2](#).

[0029]By performing each of above-mentioned pretreatments to near-infrared diffuse-reflectance-spectrum data (near-infrared relative diffusion reflection spectrum). For example, the influence of external change factors, such as influence of differences between Homo sapiens (individual difference), such as penetration reflection of the near infrared ray by the aligned states of hair differing etc. and a difference of a diffuse reflection state, and a difference of the damage of hair, is reduced.

[0030]The analytical curve of the moisture content of hair is prepared using the data (amended relative diffusion reflection spectrum data) based on the near-infrared diffuse reflectance spectrum which performed the two steps of above-mentioned pretreatments, and the moisture content data measured with the aforementioned weight method.

[0031]Although there are generally methods, such as linearity multiple regression analysis (MLR, Multiple Linear Regression) and main-ingredients regression analysis (PCR, Principal Component Regression), as the statistical work technique at the time of preparing an analytical curve. In this example of an embodiment, a partial-least-squares-regression-analysis method (PLS) is used. It is known that the partial-least-squares-regression-analysis method can presume the physical property or chemical nature of a strange sample with the most sufficient accuracy.

[0032]Hereafter, the procedure of a partial-least-squares-regression-analysis method is explained.

[0033]First, physical or the formula of chemical nature presumption is explained. Generally the method (proofreading) of determining the coefficient of an analytical curve (presumed equation which presumes the moisture content of sample hair with a strange moisture content) from the near-infrared data obtained by the exposure of the near infrared of a 1100-2500-nm wavelength band comprises the stage of a data compression and proofreading revolution. The following processings are performed using a computer.

[0034]The spectrum data of sample hair and a sample being physical and chemical nature are expressed as follows.

[0035] $X = Ix + TP + E$ -- (1)

$C = Ic + TQ + f$ -- (2)

the average value of matrix I : unit matrix x : X of the value of the inside of an upper type, and the spectrum of the sample i in the $X = \{x_{ik}\}$: wavelength k -- row vector
 $T = \{t_{ik}\}$: revolution factor procession (marks procession) of k dimension
 $P = \{p_{ik}\}$: Near-infrared load procession $E = \{e_{ik}\}$: error $C = \{c_{ik}\}$: It is the average value of physical or chemical nature c : C , and is a row vector of k dimension. by sequence vector data compression showing a $Q = \{q_{ik}\}$: chemicals load procession $f = \{f_i\}$: error. The near-infrared load procession P and the revolution factor procession T are defined, by proofreading revolution, the chemicals load q is acquired using the revolution factor procession T , and C is called for.

[0036]Next, the basic algorithm of a partial-least-squares-regression-analysis method is explained. 1. Physical as the near-infrared spectrum data matrix X of the sample of proofreading plurality or symmetrize the vector c of chemical nature first.

[0037] $U = X - Ix$ -- (3)

$Nu = c - Ic$ -- (4)

The following procedures (a), (b), (c), and (d) are performed to each factor $a = 1$ shown below, 2 --, and A . (a) Presume the near-infrared load vector p_a with a least square method (LS, Least Squares) from a following formula (5) using the chemicals

remainder nu.

$$[0038]U = nu \text{ Pa} + E \quad -- (5)$$

It normalizes to the length 1 and a solution is expressed with a following formula (6).

$$[0039]Epa = k \text{ nu}'U \quad -- (6)$$

Epa expresses the point estimate of pa among an upper type, and k is a scale factor which sets the length of Epa to 1. (b) Presume revolution factor Eta by LS from a following formula (7) using this Epa. That is, revolution factor Eta is expressed with a following formula (8).

$$[0040]U = ta \text{ Epa} + E \quad -- (7)$$

$$\text{Eta} = U \text{ Ep}'a \quad -- (8)$$

(c) Presume the chemicals load vector q by LS from a following formula (9) using this revolution factor procession ET= {Et1, Et2, --, Eta}.

$$[0041]nu = ETq + f \quad -- (9)$$

ET is a presumed revolution factor procession of T among an upper type. Therefore, a following formula (10) is obtained.

$$[0042]$$

$$Eq = (ET'ET)^{-1} ET'nu \quad -- (10)$$

It is among an upper type and ET' is an inverse matrix of (ET'ET) the transposed matrix of ET, and (ET'ET)⁻¹. (d) the new remainder U expressed with a following formula (11) - and calculate nu expressed with a following formula (11).

$$[0043]U = X - Ix - ET \text{ Ep} \quad -- (11)$$

$$Nu = c - Ic - ET \text{ Eq} \quad -- (12)$$

On the other hand, the next Epa, Eta, Eq, and the new remainder U are presumed by a procedure (a), (b), (c), and (d), and it calculates repeatedly to a=A. Eq is calculated to each a. The number A of factors is determined from the accuracy of physical or presumption of chemical nature of a strange sample or the sample for proofreading. 2. With the strange sample hair of a moisture content, Et1 can be found with a following formula (13) from (3) and (8) types, and physical or the chemical nature Eci is further determined by the following formula (14).

$$[0044]Eti = (xi - x) \text{ Ep}' \quad -- (13)$$

$$Eci = c + Eti \text{ Eq} \quad -- (14)$$

The near-infrared error Eei of standard sample hair is expressed with a following formula (15).

$$[0045]$$

$$Eei = xi - (x + Eti \text{ Ep}) \quad -- (15)$$

By the processing using the partial-least-squares-regression-analysis method explained above, by the conventional technique, what was summarized to the error term is separated as an operation between ingredients, and as a result of an error term's becoming small, an effective highly precise analytical curve is acquired. The acquired analytical curve is shown in [drawing 4](#). The analytical curves of [drawing 4](#) were 90 data numbers as mentioned above, and the correlation coefficient was 0.994.

[0046]Although the above explanation did not describe, to compensate for preparing the sample group for analytical curve creation which extracts much standard sample hair and with which analytical curve creation is presented, 90 arbitrary standard sample hair was classified from such standard sample hair, and the sample group for verifying the validity of an analytical curve was prepared. And about the sample group for this verification, in

order to verify the validity of the analytical curve prepared in the above-mentioned procedure, while measuring the moisture content with the weight method, the relative diffusion reflection spectrum was measured by near-infrared spectroscopy, and the moisture content was calculated using the above-mentioned analytical curve.

[0047]Correlation with the moisture content (moisture content predicted value of the inside of drawing 5 and a horizontal axis) measured by this near-infrared spectroscopy and the moisture content (moisture content measured value of the vertical axis in drawing 5) measured with the weight method was searched for.

[0048]The correlation formula for which it asked from the scatter chart of data and data at this time is shown in drawing 5. The correlation coefficient (r) was 0.993 and the standard error (below Standard Error: displays it as SEP.) of the correlation formula for which it asked from identity data was 0.460. SEP is expressed with a following formula (16).

[0049]

$$SEP = \sqrt{\frac{\sum (x_p - x_L)^2}{n-1}} \quad (16)$$

Inside of an upper type, n: Sample number xp : The point estimate by calculation, and here, it is the moisture content predicted value xL : Measurement (lab measurement) in a laboratory A value and here by moisture content measured value reference, The result of having asked for the correlation formula like the above about the analytical curve which changed and acquired the conditions of pretreatment of a relative diffusion reflection spectrum is shown in drawing 6. It is the sample number n= 90, respectively. "O" shows the case where the pretreatment concerned is carried out, among drawing 6, and "x" shows the case where the pretreatment concerned is not carried out.

[0050]Drawing 6 shows that the analytical curve of the case of the number 5 which carried all of three pretreatments out, i.e., this example of an embodiment, has the highest accuracy.

[0051]In the measuring method of the hair moisture poured on this example of an embodiment following on the above-mentioned analytical curve creation process, the moisture content of a test subject's hair is measured using the analytical curve of this above-mentioned example of an embodiment (moisture content measuring process). Hereafter, a moisture content measuring process is explained.

[0052]In the conditions same with having carried out, when preparing the above-mentioned analytical curve, and a procedure, it irradiates with a near infrared ray directly to a test subject's hair, and asks for near-infrared spectrum data. And the moisture content of hair is measured using an analytical curve. If analytical curve data is beforehand stored in the memory of the microcomputer of a near-infrared spectroscopic analysis device and the near-infrared spectrum data of a test subject's hair is inputted into a microcomputer at this time as described above, The value of the moisture content obtained with reference to analytical curve data is outputted from a microcomputer.

[0053]The measuring method of the hair moisture concerning this example of an embodiment explained above, What is called nondestructive measurement that does not have to carry out cutting extraction of the hair before measurement can be performed, Not the relative comparison of a moisture content but an absolute value moisture content can be measured, and the amount of mean moisture of the whole hair instead of local measurement, such as near the surface of hair, can be measured, and these measurement can be measured by a simple method further again using a simple device.

[0054]Therefore, while it is useful in the research section which develops the cosmetics for hair, in order to advise on a kind, directions, etc. of the cosmetics which fitted the individual to the cosmetics user at the shop front of cosmetics sale especially, it is effective when grasping the moisture state of a cosmetics user's hair.

[0055]The result of having measured the moisture content of the hair of five test subjects (it expresses as the numbers 1-5 among drawing 7) from whom the grade of the damage of hair differs next using the measuring method of the hair moisture concerning this example of an embodiment is shown in drawing 7. The moisture content by this method is a moisture content of the hair measured by near-infrared spectroscopy among drawing 7, and the moisture content by an exception method is a moisture content of the hair measured with the weight method.

[0056]According to the measuring method of the hair moisture concerning this example of an embodiment, from drawing 7, it was checked that a moisture content can be measured by accuracy of measurement practically sufficient also about the hair of the grade of various damages.

[0057]The measuring method of the hair moisture concerning this example of an embodiment has being influenced [less] by external change factors, such as a damage of hair, than the above.

[0058]As this example of an embodiment described, when acquiring a near-infrared spectrum, it has influence of external change factors, such as influence of individual difference (solid difference), and a difference of the degree of damage of hair, as a factor which affects measured value. And in this example of an embodiment, the influence of these factors is randomized by performing a statistical work and preparing an analytical curve.

[0059]On the other hand, for example, based on the shift amount beforehand calculated about each element of external change factors, such as a grade of the damage of hair, atmospheric temperature, humidity, amend near-infrared spectrum data, and the spectrum data of the imagination for every external change factor is created, The analytical curve for every value of an external change factor may be prepared with the spectrum data of this imagination.

[0060]

[Effect of the Invention]The analytical curve creation process of according to the measuring method of the hair moisture concerning this invention irradiating with a near infrared ray to two or more hair samples of moisture content known, asking for two or more diffuse reflection or penetration reflection spectrum data, and preparing the analytical curve of the moisture content of hair, Since it has a moisture content measuring process which irradiates with a near infrared ray directly to a test subject's hair, asks for diffuse reflection or penetration reflection spectrum data, and measures the moisture content of hair using an analytical curve, What is called nondestructive measurement that does not have to carry out cutting extraction of the hair before measurement can be performed, Not the relative comparison of a moisture content but an absolute value moisture content can be measured, and the amount of mean moisture of the whole hair instead of local measurement, such as near the surface of hair, can be measured, and these measurement can be performed by a simple method further again.

[0061]In [according to the measuring method of the hair moisture concerning this invention] an analytical curve creation process, Pretreatment which prepares an

analytical curve using a partial-least-squares-regression-analysis method, or differentiates a predetermined degree again to two or more diffuse reflection or penetration reflection spectrum data, And the moisture content of hair can be measured in high accuracy, without receiving influence in external change factors, such as a damage of hair, since the stage of performing at least one pretreatment in pretreatment which gives MSC is included in two or more diffuse reflection or penetration reflection spectrum data.

[Translation done.]